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observations; and we seem, therefore, entitled to conclude that the diurnal movements of the two horizontal magnetometers are accounted for by electric currents traversing the upper strata of the earth.

There is one point of difference, to which it important to draw attention. It will be seen that the calculated curves are, for the most part, above the observed. The reason of this will be evident upon a little consideration. The zero from which the calculated results are measured is the mean of the day; whereas that of the observed results is the true zero, corresponding to the absence of all current. Now, the chief deflections of the galvanometer needle (as appears from the latter curves) are those in which the sun is above the horizon; and the zero line, consequently, divides the area of the diurnal curve unequally, being considerably nearer to the night observations than to those of the day. If the calculated curves be displaced by a corresponding amount, their agreement with the observed will be much closer.

The difference here noted is one of considerable theoretical importance. Magnetometric observations furnish merely differential results, the magnitude and the sign of which have reference solely to an arbitrary zero. We are accordingly ignorant even of the relative values of the effects, and are unable to compare them with their physical causes, whether real or supposed. In these respects the galvanometric observations have the advantage. In them positive and negative are physically distinguished by the direction of the currents; and this, as well as the absence of all currents, is indicated by the instrument itself. The results, therefore, furnish the measures of the forces by which they are produced.

The next, and most important, step in this inquiry will be to assign the physical cause of these phenomena. The existence of electric currents traversing the earth's crust has hitherto been maintained as an hypothesis, on account of its supposed adequacy to explain the terrestrial magnetic changes. Now, however, their existence is proved, not only to be a fact, but also a fact sufficient to explain the phenomena. It remains, therefore, only to ascertain their source; and it will be for those who deny that the sun operates by its heat in producing the phenomena of terrestrial magnetism, to assign to these currents a more probable origin.

PROFESSOR WILLIAM K. SULLIVAN read the following paper, written by himself and Joseph P. O'REILLY, C.E.:—

On the Hydrocarbonates and Silicates of Zinc of the Province of Santandee, Spain.

GEOLOGICAL CONDITIONS UNDER WHICH THE ORES OF ZINC OCCUR.

The district of country comprised by the province of Santander lies between the prolongation of the Pyrenees, which, under various names, traverses the north of Spain, and the Bay of Biscay—the mountains forming

its southern boundary, and the sea its northern. It adjoins the province of Biscay on the east, and that of Asturias on the west. The first range of the chain forming the southern boundary of the province, which at Puente Viesgo is only a few miles from the coast (four leagues from Santander, the chief town), is chiefly formed of mountain limestone. Upon this rock rest beds of red sandstone, and ochry clay, with accompanying gypsum; these are succeeded by shelly limestone, sandstone, and clay, irregular beds of limestone, and dolomite, some of which yield an excellent cement. Upon these rocks rest beds of shelly limestone, and of dolomite, the former containing abundance of a large species of ostrea, and of terebratulæ and ammonites. Above these, on the sea-coast, tertiary limestone and sandstones are found. The rocks which thus occur between the mountain limestone and the tertiary beds apparently represent the two lower groups of the triassic period—the bunter sandstone and the muschelkalk. For the moment this opinion is little more than a guess; but we hope to be able to establish the true relations of all those beds, when we have collected the materials for a memoir upon the geology of the entire district, with which we propose to occupy ourselves.

In the mountain limestone at Viesgo are found galena, blende, carbonate of zinc (Smithsonite), copper and iron pyrites, with here and there deposits of gypsum. The hot baths of Viesgo, Las Caldas, and Thermida, indicate the probable proximity of igneous rocks, or, at all events, the existence of conditions favourable to metamorphic action. Indeed, the limestone in the immediate vicinity of a lead lode which occurs in this rock is hardened into marble. The lodes occur generally not far from the line of junction of the limestone with the red sandstone. In the soft steatitic clay which is found in the lodes, abundance of doubly terminated crystals of clouded quartz are found. Small crystals of the same kind, imbedded in a paste of peroxide of manganese, likewise occur in the lodes. There is, indeed, everywhere in the district, evidence of the presence of large quantities of silica in solution, in former times. The vein stone is sulphate of barytes, or calcite; the latter is frequently found in large crystals, of the form of a scalenohedron (the metastatique of Hauy, d_2 of Levy and Dufrenoy, and S_3 of

Ores of zinc likewise occur in the newer or triassic rocks. Their chief seat is the dolomite, which, if our surmise be correct, belongs to the muschelkalk, and suggests analogies with the zinc deposits of Wiesloch in Baden. The ores which occur are blende, often galeniferous, and carbonate (Smithsonite), the latter being most abundant. The lodes are usually vertical, traversing the dolomite nearly at right angles, and presenting generally merely the elements of a lode or vein, namely, a plane of fracture with some foreign matter interposed, which, as in the mountain limestone, is usually sulphate of barytes and calcite, the small rhombohedral crystals of the latter being in some places altered into sulphate of barytes. In some cases, as will be noticed presently, the calcite is replaced by carbonate of zinc, which forms beautiful pseu-

domorphites of the calcite in the form of scalenohedrons. At the mines which have been worked near Ciguenza, a village about five miles east of Santander, the thickness of the lode is variable, increasing at the points where ore, especially carbonate, occurs, to 1^m or 2^m, but diminishing to an inch where this mineral disappears, or is replaced by blende. Sometimes all ore disappears, so that the lode is only represented by a band of barytes, or calcite.

In the district just named, several lodes run east and west nearly parallel, and can be traced over a length of about 1000^m in the dolomite, beyond which, though doubtless they extend much further, it is difficult to trace them, in consequence of the nature of the ground. Some of the lodes consist of a rib of carbonate of zinc, sometimes galeniferous, of varying thickness, encased in very light friable ochry clay, looking like decomposed dolomite. In others, the ore consists of carbonate and blende, the latter forming the centre rib.

The carbonate of zinc, or Smithsonite, found in these lodes, is generally very cavernous, or rather what may be termed clinkery, the walls of the empty spaces being frequently lined with small crystals of the same The ore is usually yellowish-brown; it is also found as a mineral. yellowish-white compact mineral, resembling the dolomite in appearance, in very dense calcedony-like semi-translucent masses of a pale yellow colour, passing into white, the surfaces of which have a reniform structure, in stalactitic forms, and as a friable, and more or less compact earthy mineral, associated with blende. The blende from the higher ranges, such as the mountains of Europe, is comparatively free from iron, and is frequently found of a sulphur-yellow, or pale garnet-red colour, and beautifully transparent. This blende decomposes into pure white Smithsonite, which is sometimes compact and dense, and sometimes in friable earthy masses; when broken, some unaltered blende is often found in the centre of pieces of this kind of carbonate. An earthy pale buff-coloured dolomitic-looking carbonate of zinc, associated with earthy cinnabar, is found in the same locality; this is obviously derived from a less pure variety of blende, mixed with cinnabar, which occurs there. We also meet with a granular crystalline form of Smithsonite, of a pure white colour, or tinged with a pale lemon-yellow or rose.

The blende occurring in the limestone, and especially that in the dolomite, is ferruginous, and in some cases appears to decompose with great facility into Smithsonite.

When the blende from which the Smithsonite is derived is associated with galena, the latter is very commonly found unaltered in the carbonate of zinc. It appears, however, to have sometimes undergone decomposition; for crystals of carbonate are found abundantly in Smithsonite from Puente Viesgo, from the Venta mine near Comillas, and from the mines of Celis (three leagues south of San Vincente de la Barquera), and no doubt would be found in all galeniferous Smithsonite from the district. Specimens may often be found containing galena, blende, and carbonates of lead and zinc. The existence of lodes of pure white carbonate of lead, known to, and extensively worked by the

Romans in this part of Spain, seems to show that at some former epoch the decomposition of metallic sulphides, and the formation of carbonates, must have taken place under very favourable conditions. That the change still goes on, is perfectly shown by specimens of brown ferruginous blende from the mines of St. Felix and St. Lucita, near Comillas; in these specimens the decomposition of the blende into friable earthy carbonate has proceeded regularly from without inwards, most

specimens still containing a nucleus of unaltered blende.

The calcedonous yellow and white Smithsonite already spoken of, and which is so abundantly found at the Merodio mines, near Comillas, in reniform and botryoïdal masses, must have been deposited from solution. This opinion is corroborated by the circumstance that, in the same mine, the calcite vein stone enclosing blende, has been in great part substituted by carbonate of zinc. One of the resulting pseudomorphites has the form of the scalenohedron, called by Hauy the metastatique; and although not quite half a complete form, the terminal edges, which are well defined, are nine centimetres long. It is a shell of from 3 to 5 mm thick of semi-translucent Smithsonite, which is partially filled up with a warty tufaceous mass of the same substance. The inner side of the shell, in the part not filled up, is covered with a number of small warts. Whenever one of these more or less hollow pyramids is unbroken, a small hole may be observed in the end, where it is broken off from the wall of the druse; through this the lime was removed, and the tufaceous zinc introduced. A similar hole may often be seen in large crystals of felspar, which have been decomposed in the inside, or in a tooth in the first stage of decay.

This association of compounds of iron with those of zinc is interesting, especially in connexion with the minerals which form the subject of this paper. In the capping of dolomite forming the south side of the valley of Ciguenza, which has been formed by the removal of the dolomite, and the laying bare of the underlying limestone by denudation, occur several lodes, to which allusion has been already made. One of these has been worked for galeniferous carbonate at a mine called "Emilia," while at another mine called "Vicenta," to the westward upon the same lode, the ore found was almost pure carbonate. Upon sinking a mine in one of the parallel lodes about 30^m north of the principal lode at Emilia, only iron ore similar in appearance to the calamine was found; at the depth of five or six metres this passed into pyrites, but blende was not found. The continuation of the same lode to the westward, near the mine Vicenta, gave, on the other hand, an earthy ore of iron mixed with blende, and at a greater depth pyrites,—the ore consisting at this point of a rib, one side of which was pyrites and the other blende. Still deeper the iron disappeared, and was replaced by carbonate of zinc, exactly as in the neighbouring part of the main lode.

It would thus appear that the iron ore is the result of the decomposition of pyrites. In this case, a large quantity of sulphuric acid must have been formed and removed, and must have contributed to the de-

composition of the associated blende, and perhaps to the formation of hydrocarbonate of zinc—a mineral which heretofore was known to occur only in small quantities, but which has been formed in very large quantities indeed in this district.

The hydrocarbonate of zinc is chiefly found in the limestone underlying the dolomite. The most remarkable deposit of it is that which occurs at a mine called Dolores, in the valley of Udias. As this deposit is interesting from several points of view, a description of the circumstances under which it occurs will, while offering several peculiar features, explain the general conditions under which all the similar deposits are found. The northern escarpment of this valley presents the following ascending succession of rocks:—

- 1. Red sandstone and clay beds, with accompanying gypsum.
- 2. Very shelly limestone.
- 3. Sandstone and beds of clay.
- 4. Irregular beds of limestone and dolomite,—the under bed producing a good hydraulic lime.
 - 5. Shelly limestone, containing abundance of oyster-shells.
 - 6. Dolomite.
 - 7. Tertiary limestone.
 - 8. Tertiary greenish sandstone.

There appears to be a fault in the direction of the axis of the valley through which a stream runs, which has produced a downthrow on the south, equal to the thickness of the upper beds of No. 1, and the whole thickness of Nos. 2 and 3; so that the bed of limestone producing hydraulic cement has been brought in contact with red sandstone of the northern side.

The dolomite contains yellowish-red Smithsonite, while the subjacent shelly limestone contains the hydrocarbonate associated with silicate of The ore is irregularly dispersed in the spaces between the planes of stratification, and in the vertical joints. The beds of limestone have only a very feeble dip,—not more than from 10° to 15°. The joints are very regular, and nearly vertical to the plane of bedding; so that each bed is not unlike a great pavement, in which ablock gives way, if not directly sustained by the subjacent bed; hence, caverns are easily formed in such a rock. A shaft was sunk into this rock near its junction with the dolomite, and a depth of about 10^m to 12^m had been attained, when the workmen came upon an opening into such a cavern; and on descending into it, they discovered some fossil bones upon the floor, among which were recognised some teeth of an elephant in an excellent state of preservation, and some broken antlers. This interesting circumstance led one of us (Mr. O'Reilly), in company with M. Javot, the head engineer of the mines, to visit the cavern. On descending into it, the visitors were struck by the appearance of the roof and floor; from the former descended stalactites of various sizes, and of most fantastic forms, the most common being that of an elongated inverted cone, like those met with in limestone caverns; many, however, presented the appearance and colour of white coral trees, and some, being composed of hydrocarbonate of zinc, were of the dazzling white colour peculiar to that mineral.

The floor was composed of one immense bed of white hydrocarbonate of zinc, of variable thickness, but in some places it was found to attain a thickness of 1^m 5,—the irregularity of the ground producing a corresponding irregularity in the surface of the bed. Traces of a stream were recognised, which during the rainy season traverses the cavern, and which, no doubt, contributed to the deposition of the hydrocarbonate of The floor was so white, that the visitors hesitated to tread upon it with their muddy boots. Here and there the floor was covered with the mineral in a granular form, and portions of it upon which water was continually falling felt soapy. The phenomena presented where the dropping occurs are very interesting, and differ materially from what are observed during the ordinary formation of stalag-The running water accumulated during a period of rain had apparently deposited gradually a thin layer of hydrocarbonate, the soft surface of which became exposed to the action of the water dropping from above, as soon as the supernatant water had drained away. immediate consequence of the fall of the first drops was the formation of a cup-shaped cavity. The dropping water contained some silicate in solution, which immediately produced a gelatinous compound with the zinc of the floor. The splash of the drop upon the soft gelatinous matter threw small globules of it about. Similar little globules of soft hydrocarbonate, free from silica, appear to have also been formed in the same way. As the cup enlarged, several of these globules became enlarged by the gradual deposition of successive layers, and, remaining in the cup, got moved about, and had their surfaces polished whenever a rapid succession of drops fell. A rapid succession of drops, not accurately falling upon the same spot, seems to have detached fragments of the more or less soft mass, or floods of water may have carried broken fragments of the mineral into the cups; and being too large to be ground into round fragments, they were into flat lenticular or irregular pebbles. The cups thus formed were filled up by the successive deposits of mineral matter which floods brought into the cavern. But while on the level floor the hydrocarbonate was deposited in successive laminæ, the cups became the moulds of concretions. In this way, probably: the cup got filled up with soft mineral; as the water drained off, drops began again to fall into the centre of the soft mass, by which a fresh cup was produced, and this again filled up, and so on; the final result being the production of a kind of flattened spheroidal concretion, with a slight indentation in the Sometimes the points from which the drops fell appear to have changed, so that no new cup was formed. In this case, the last deposited matter contracted on drying, and left a slight depression, with irregular lips, not unlike an opening bud. The change in the point from which the drops fell was often very slight, so that a new cup was formed close to, but not directly over, the first one; or droppings took place at the same time from two points, so close as to produce twin cups.

The rounded particles formed by the droppings acted as the nuclei around which deposits took place, so that they often became enlarged from the size of a peppercorn to that of bullets, or larger. When a number of these got imbedded in the soft mineral mud, a pisolithic mass was formed. Some of the balls, however, contain so large a nucleus of the translucent opal-like compounds of silicate and carbonate of zinc, to be described further on, that we must suppose them to have been formed by the falling of large drops of water holding silicates in solution into a solution of hydrocarbonate of zinc.

The fossil bones lay on this floor, partially or wholly enveloped in the hydrocarbonate. The greater part of the collection has been transferred to some Spanish museum, so that, for the present, we cannot give any particular account of them. A few fragments, however, having fortunately come into our hands, an opportunity was afforded of making a chemical examination of them, with a view of determining how far a substitution of lime by zinc took place. The results will be found further on.

The under side of a piece of the floor, in which a bone completely enveloped in hydrocarbonate was partially buried, was composed of a kind of conglomerate of flattened, and more or less rounded, fragments of hydrocarbonate of zinc, evidently the result of the action of running wate. They were, in fact, the pebbles of a stream upon which the bones rested, and which were cemented by hydrocarbonate, and then covered over, and the bones more or less buried in the successive layers of hydrocarbonate of zinc deposited in comparatively still water.

The hydrocarbonate of zine is found in compact earthy masses of a pure white colour, or slightly coloured brown by organic matter, and more or less distinctly laminated, as a friable bergmehl-like sinter, as stalactites, concretionary nodules, pisolithic masses, &c. It is usually associated with silicate of zinc, which is found coating it in small crystals, or in layers composed of colourless translucent fibrous crys-Sometimes these layers alternate with the hydrocarbonate; even when the fibrous silicate occurs in concretionary masses of considerable thickness, each layer appears to be separated by an extremely thin opaque parting of hydrocarbonate of zinc. Layers of hydrocarbonate are often found having the fibrous structure of the silicate, but containing no silica. They may possibly be the result of pseudomorphic action, and consequently to be regarded as pseudomorphic hydrocarbonate after fibrous hydrated silicate of zinc. This intimate association of hydrated silicate of zinc and hydrocarbonate of zinc extends much further than mere mechanical associations; for in the balls already mentioned we shall find examples of combinations of the two in various proportions, and even the pure fibrous silicate will be shown to contain carbonic acid.

The preceding observations indicate the chronological order in which the different kinds of zinc ores in the province of Santander have been formed. The primitive ore was blende, associated generally with more or less pyrites; the decomposition of the blende produced the Smithsonite. Contemporaneously, as it appears, with the transformation of blende, water holding some salt, or perhaps several salts, of zinc in solution percolated through the joints, and between the planes of bedding of the limestone underlying the dolomite—chief seat of the Smithsonite—and deposited there, and in the caves formed in the limestone the masses of hydrocarbonates now found there. The proper discussion of the chemical changes by which these minerals have been formed, involves the solution of several chemical problems, such as the action of solutions of bicarbonates upon those of sulphate of zinc, the action of sulphate of protoxide of iron upon sulphide of zinc, &c. One of us has already begun the investigation of these problems. We may therefore defer until its completion any attempt to trace out the successive transformations by which the Smithsonite and hydrocarbonate were formed.

The occurrence of the bones partially buried in the hydrocarbonate of zinc forming the floor of the cavern above described, affords a test by which to determine the exact geological age of the deposits of hydrocarbonate, and consequently of the formation of the greater part of the Smithsonite. This test is the more valuable, because evidence showing the period of geological time to which the deposition of the contents of mineral veins belongs is very rare. There can be no doubt that the deposition of the greater part of the hydrocarbonate was contemporaneous with the existence of the species of animals to which the bones belonged. It is probable, therefore, that the deposition of that mineral in the cavern began during the pleistocene period, and has continued down to the present time. Until an opportunity is afforded of making an accurate examination of all the bones, this conclusion must, however, be looked upon as provisional.

Effect of the Zinc Solutions on the Fossil Bones. - Before passing to the discussion of the chemical composition of the hydrocarbonate of zinc and the associated silicates, it may be interesting to notice the effect which the solution of a salt of zinc has had upon the composition of the bones. Only a few of the bones found came into our possession, and they were chiefly fragments. Some were wholly enveloped in the white mineral, others only partially. Among the latter was a tibia, apparently belonging to some ruminating animal—probably a large-sized deer. This bone had lain on the floor, and was covered from time to time with water holding a salt of zinc in solution, whenever the cave was flooded. On one side was a partial stalagmitic coating, apparently produced by droppings from the roof. It was beautifully white; the dense part of the bone adhered strongly to the tongue, like burnt bone; it was, however, much more fragile, and friable. Even when kept for several days over oil of vitriol, it lost a considerable quantity of water, which appeared to be chemically combined with it. The cancellated tissue of this bone was beautifully preserved. A portion of this tissue was put for three or four days into acetic acid diluted with about twice its weight of water, in order to dissolve out the carbonates which it contained; this

process was repeated once with fresh acid, somewhat stronger, so as to insure the total removal of the carbonates. Sulphide of hydrogen in excess, added to the acid solution, gave a copious precipitate of sulphide of zinc; this was removed by filtration, and oxalate of ammonia added to the filtered solution, which threw down a precipitate of oxalate of This shows either that the whole of the carbonate of lime was not removed from the bone during the action of the solution of zinc, or that new carbonate of lime had been formed from the phosphate by the substi-The tissue treated with the acetic acid was tution of oxide of zinc. washed repeatedly with distilled water, and boiled with it, in order to remove all traces of the acetates of zinc and lime, and then dissolved in hydrochloric acid. To this solution ammonia was added in excess, and it was then digested for some hours, so as to insure the re-solution of all the phosphate of zinc thrown down at first. On filtering, the phosphate of lime remained on the filter; the filtered liquid contained any zinc existing as phosphate; on adding sulphide of ammonium to the solution, a precipitate of sulphide of zinc was thrown down. The solution filtered from the precipitate of sulphide of zinc, treated with chloride of magnesium, gave a precipitate of ammonio-magnesian phos-On determining the amount of zinc in the precipitated sulphide in the usual way, and calculating the amount of phosphoric acid in the ammonio-magnesian phosphate, the results showed that the phosphoric acid and oxide of zinc were in the proportions to form the salt 3ZnO,PO₅. In the air-dried bone, the amount of oxide of zinc as phosphate was 6.090 per cent., equivalent to 10.805 per cent. of 3ZnO, PO₅. The amount of lime thus substituted by zinc appeared to vary according as the bone was completely enveloped or not, and according to the part of the bone examined. The solid part of a fragment of a small bone, completely enveloped by a coating of hydrocarbonate about 5mm thick, contained a quantity of oxide of zinc equivalent to 16.98 per cent. of phosphate of zinc. A part of the carbonate of lime may have been derived from this substitution. Scarcely a trace of the organic matter of the bone had been preserved, but in those which were covered by layers of hydrocarbonate, the inside of the coating or shell of mineral, when removed from the bone, had always a vellowish-brown superficial colour, and bore an accurate imprint of the bone. When the inner layer of such a coating was dissolved slowly in moderately dilute acetic acid, brown membranaceous flocculi floated about, which were probably the remains of the periosteum. This would seem to show that the bones were not much decayed before they were enveloped in the hydrocarbonate of zinc, and consequently confirms the view that the formation of the upper layers, at least, of the hydrocarbonate of zinc in the cavern, was contemporaneous with the species of animals to which the bones belong.

Chemical Composition of the Hydrocarbonate of Zinc.—Analyses of the Spanish hydrocarbonate of zinc have been already published by MM. T. Petersen and E. Veit*, and by M. A. Terreil.† The former believe that

it has not a constant composition. The mean of several analyses of a portion taken from the centre of a large piece gave,—

		Calculated.			Found.
ZnO,		73.021			73.1
CO ₂ ,		14.838			15.1
HO,		12.140			11.8
				_	
		99.999			100.0

The calculated percentage is derived from the formula 8ZnO,3CO_v 6HO. Exposed to the air for three months, its composition was found to be:—

			Calculated.			Found.
ZnO,			$75 \cdot 277$			74.73
CO ₂ ,			13.597			13.81
ΗО,			11.124			11.45
			99.998			100.09

The calculated numbers are here derived from the formula 3ZnO, CO₄,2HO, which they assign to it.

The following are the results of an analysis of a ball of hydrocarbonate, made by M. Terreil:—

ZnO,												68.15
CO ₂ ,												13.17
CaO,												1.60
Al ₂ O ₃	Fe.	О3,										0.80
НО,												12.40
Hygr	osco	opic	W	ateı	٠,							3.13
Organ	ic 1	mat	ter	cor	itai	nin	gr	itr	oge	n,		traces
_							-		-			
												99.25

This corresponds, according to him, to the formula 5ZnO, 2CO₂, 3HO; but as part of the water is hygroscopic, he prefers the formula 3ZnO, CO₂, 2HO. If we deduct the lime, alumina, iron, and hygroscopic water, and calculate the composition of the remainder in 100 parts, and also calculate the theoretical composition in 100 parts from the formula 3ZnO, Co₂, 2HO, we get the following numbers:—

		(Calculated.			Found.
3ZnO*,			$75 \cdot 277$			72.716
CO ₂ ,			13.597			14.052
2H0,			11.124		٠	13.230
			99.998			99.998

^{*} Equivalent of Zinc = 32.6.

These numbers differ too much to warrant us in accepting the for-

mula proposed by M. Terreil as the true one.

M. Terreil states, that even at 200° cent. hydrocarbonate of zinc loses only hygroscopic water; this statement appears singular, especially when we recollect the interesting results of M. Damour,* who found that even the zeolites, with the exception of analcime, possess the property of losing considerable quantities, and sometimes even the whole of their hydrated water, either when placed in a perfectly dry atmosphere, or when exposed to temperatures comprised between 40° cent., and incipient redness, and of again taking it up. The loss of water which hydrates sustain when heated, depends not only upon the temperature to which they are exposed, but likewise upon the relative facility with which the air in contact with them is changed, and upon the duration of the exposure. In order to test this point, the percentage of water and carbonic acid in a piece of perfectly white compact hydrocarbonate was determined by the loss which it sustained by ignition, in its airdried state, after an hour's exposure to a temperature of 130° cent. in an oil-bath, and after an exposure of five or six hours to a temperature ranging between 150° to 180° cent., and with frequent exposure to the air. A similar experiment was tried with a fragment of pure white friable bergmehl-like hydrocarbonate. The following table contains the results of these experiments:—

	Compact	F	riable light
	Mineral.		Mineral.
Total HO, and CO2 in air-dried mineral,	25.738		28.380
Loss in one hour at 130°,	2.041		3.151
Loss in six hours at 150° to 180°	14.423		18.571

The following table represents the relative composition at each stage:—

		ompact Mine	Friable light Mineral.					
	Air-Dried.	Dried at 130°.	Dried at 150° to 180°.	Air- Dried.	Dried at 130°.	Dried at 150° to 180°.		
			. 88.898 —					
HO,	. 25.738 .	. 24·191	. 11·102 —	28.380 .	. 23.879 .	. 7.689		
	100.000	100.000	100.000	100.000	100.000	100.000		

These experiments show that not only does hydrocarbonate of zinc lose hydrated water at temperatures under 200°, but even a considerable quantity of carbonic acid. It is even probable, that in a current of hot air at a temperature of 180° cent., it would be fully decomposed. It may, however, be safely dried at the temperature of boiling water, or even as high as 120° cent., provided it be not too long exposed to the heat.

With the view of determining whether the composition of the hydrocarbonate is always constant, a large number of specimens, exhibiting

^{*} Compt. rend. t. xliv. p. 975.

as great a variety of structure and origin as possible, were examined In some cases the sum of the water and carbonic acid was determined by ascertaining the loss by ignition; but in several cases every constituent was separately determined, and great care was especially taken in estimating the amount of carbonic acid. The following contains the description of the specimens, and the results of the analyses:—

I.—Compact indistinctly laminated mass, with its upper surface covered with ripple marks; colour, pure white, opaque; dull, earthy, but with a slightly conchoidal fracture, and fissile along the planes of deposition; somewhat brittle, streak shining. Hardness = 2. Specific gravity, 2·232, or 3·758 after it has become fully saturated with moisture. The piece examined was taken from the centre of the mass, which was twelve centimetres long, ten wide, and eight thick.

II.—Fragment taken from the exterior of the last-mentioned mass,

which had been many months exposed to the air.

III.—Light, porous, friable mass, of a perfectly white colour, and not unlike some kinds of meerschaum, but much more friable, being easily reduced to powder between the fingers.

IV., V., VI.—Specimens of compact white hydrocarbonate, similar to I. and II.

VII.—Compact white hydrocarbonate, very distinctly laminated, and slightly discoloured from clay, &c., on the surfaces of the laminæ; formed part of the floor in which the bones were buried.

VIII.—Another specimen of light, friable sinter, similar to III.,

but having a faint rose-red tint.

IX.—Fragment of the hydrocarbonate encasing a piece of bone. Some of the layers, though perfectly opaque, had a fibrous structure, like silicate of zinc.

X.—Part of a lump of pure white compact hydrocarbonate, enclosed in translucent crystalline Smithsonite.

XI.—Part of a lump of pure white compact hydrocarbonate, intermixed with white transparent fibrous silicate of zinc.

XII.—External layer of a stalactite, having a distinctly fibrous structure, analogous to that of the silicate.

XIII.—Ball of white hydrocarbonate of zinc, one centimètre in diameter.

I,				11.				III.	
74.059				74.244				73.581	
0.011				0.013				0.010	
0.008				0.005				0.003	
0.003				_				_	
14.934	1			14.893	ì			14.980)	
10.070	25	968		10.027	25	656	3		26.429
				0.736	}			1.028)	
traces				traces	•			traces.	
									
100.049				99.918				100.023	
	0·011 0·008 0·003 14·934 10·070 0·964 traces	0·008 . 0·003 . 14·934 10·070 25 0·964 traces .	0·011	0·011	74·059 74·244 0·011 0·013 0·008 0·005 0·003 — 14·934)	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	74.059 74.244	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

Oxide of zinc, . Carbonic acid,	1v. 74·173	v. . 74·262	vi. . 74·247	vii. . 74·092	viii. . 73·427
Hydrated water, Hygroscopic water	25.827	. 25.738	. 25.753	. 25.908	. 26.573
					
	100.000	100.000	100.000	100.000	100.000
	IX.	x.	XI.	XII.	XIII.
Oxide of zinc, .	74.232	. 74.284	. 74.391	. 74.437	. 74.480
Carbonic acid,	25.778	. 25.716			
	100.000	100.000	100.000	100.000	100.000

So far as these results go, they prove that the change assumed by Messrs. Peterson and Veit to take place in the composition of the mineral by exposure to the air does not occur. It is probable that the mineral may have been when first formed more highly hydrated, and that, according as it hardened, in consequence of the gradual evaporation of the mechanically-adhering water, it likewise lost part of its hydrated water,—thereby giving rise to the formation of a sufficiently stable compound to remain unaltered in the air. We generally consider that hydrated gelatinous precipitates have the composition which the analyses of the bodies formed by throwing them upon filters, pressing and drying the filtered masses, give us; it is, however, very probable, that the moist gelatinous mass is a different hydrate from that which we get upon the dried filter. It is quite possible that all bodies capable of combining with water may do so in a great many proportions, some of which only possess the necessary degree of stability to enable us to isolate them—of this we have a striking example in the two, if not three, hydrates which common salt forms. We also know that in bodies which contain several equivalents of hydrated water, each equivalent may not always be held with the same amount of force. All the specimens examined by us were thoroughly air-dried, having been in a dry, warm room, during more than eight months, and had all consequently arrived at the stage of greatest stability, whatever may have been the original degree of hydration. It does not appear that any carbonic acid was

If we consider the part of the water which is driven off in the water-bath as hygroscopic, the formula $8\mathrm{ZnO},3\mathrm{CO}_25\mathrm{HO}=3$ (ZnO,CO₂) + 5 (ZnO,HO), represents the composition of the Spanish hydrocarbonate. The following table, which contains the results of the analyses I., II., III., from which the hygroscopic water, lime, &c., have been deducted, shows the agreement between the composition calculated from this formula and that deduced from experiment:—

Found.

When hot or cold solutions of sulphate of zinc and carbonate of soda or potash are mingled, a precipitate is thrown down, which was analysed by Schindler, and for which he proposed the formula 8ZnO,3CO₂,6HO. This is also the formula which Messrs. Peterson and Veit deduced from their analyses of the part taken from the centre of the mass. If we considered the water driven off at 120° as part of the hydrated water, the composition of No. III. would to some extent agree with the formula—to some extent only, however, for the water, which in an air-dried specimen is more likely to be in excess, is too small. But as it is only the friable porous variety, which must contain most hygroscopic water, that agrees with this formula, while all the compact varieties differ materially from it, we could not, even if we had not positive evidence that part of the water is hygroscopic, adopt the formula of Schindler.

How are we to look upon those hydrocarbonates? Are they compounds of hydrated oxide of zinc and of carbonate of zinc, or are they basic carbonates combined with water? If the former, Schindler's formula should be written thus:—[3 (ZnO,CO₂) + 5 (ZnO,HO)] + HO; if the latter, 8ZnO,3CO₂ + 6HO. In the former case the water performs two functions, and one equivalent must be held with much less force than the other five. It is probable that the most stable hydrate of oxide of zinc, is that represented by the formula ZnO,HO; accordingly we find that, in the majority of hydrocarbonates yet discovered, the sum of the equivalents of carbonic acid and water is equal to the number of equivalents of zinc. May it not be that the body examined by Schindler was not perfectly dry; and that its real composition was 3 (ZnO, CO₂) + 5 (ZnO,HO). In this case it was identical in composition with the Spanish hydrocarbonate.

With regard to the second formula of Messrs. Peterson and Veit, which assumes not merely a loss of hydrated water, but also of carbonic acid, we believe that their conclusion is founded upon an erroneous estimation of the carbonic acid. On looking to page 14, it will be found that the amount of oxide of zinc which they found is considerably below that calculated from their formula, while it is very little above that deduced from our formula—indeed, their analysis of the part exposed to the air for three months, so far from leading to the formula 3ZnO, CO₂,2HO, fully confirms ours, as the following table, in which our analyses are contrasted with theirs, and with the theoretical composition

deduced from our formula shows :-

Calculated.	I,	II.	111.	P. & V.
8ZnO, 74.529				
3CO ₂ , 15·144 25·469 5HO, 10·325 25·469	15.075 125.210	15.020) 95.121	15.134 (25.662	13.81) 95.960
5HO. 10.325 120 405	10.165 (20 240	11.111120 101	10.528 (20 002	11.45 20 200

The original substance to which the name zinc bloom or zinc blüthe was given, and which consists of a species of efflorescence which forms on the walls of zinc mines, and upon the rubbish taken out of the workings, appears to be a different compound from that which we have been describing. Smithson first, I believe, analysed a specimen of this mineral in small mammiform patches from Bleiberg, in Carinthia. Another analysis of it was made by Dr. Carl Schnabel,* with a specimen which had effloresced upon the rubbish at Ramsbeck, in Westphalia, under the influence of strong sunshine. Similar efflorescences are found upon a curious blende, which occurs in globular and reniform masses, formed of concentric layers at the Venta, near Comillas, specimens of which we have analysed; and also upon some Smithsonite from the mines of Florida. These different specimens agree very well in composition, and may be represented by the formula 3ZNO, CO2, 3HO. The white compound which forms upon the surface of metallic zinc when moistened, and exposed to the air, appears to belong to the same category, as the following table, containing the results of all the analyses, shows :-

Calculated.	Venta.	Bleiberg (Smithson).	Ramsbeck.† (Schnabel).	Artificial Compound (Bonsdorff)
3ZnO, 71·311	71·260 28·740	71·4	$\begin{array}{c} \cdot & 71 \cdot 210 \\ \cdot 6 & 13 \cdot 677 \\ 15 \cdot 113 \end{array} $	$\begin{array}{ccc} 3. & 3. & 71.25 \\ 8.790 & 14.19 \\ & 14.56 \end{array} $ 28.750
99:998	100.000	100.0	100.000	100.00

In this formula the sum of the equivalents of carbonic acid and water exceed the number of equivalents of oxide of zine, and consequently the objections urged against Schindler's formula apply here with equal force. We had not, however, enough of the mineral to determine the carbonic acid separately, or whether a portion of the water could be driven off at a lower temperature than the rest. It would be useless to discuss the matter further until the whole of the compounds of oxide of zinc with carbonic acid and water, obtained by precipitating salts of zinc by means of carbonates, by the rusting of zinc, &c., shall be reexamined. It is interesting, however, to find that the natural compounds obtained by precipitation and by efflorescence, exhibit exactly the same difference as the artificial ones, and, furthermore, that the corresponding natural and artificial bodies are identical in composition.

Messrs. Peterson and Veit give 3.52 as the specific gravity of the Spanish hydrocarbonate of zinc; while M. Terreil gives 2.042. The following observations will, we think, explain the discrepancy. A piece of No. I., when allowed to absorb water completely, was found to have the density 3.758; the quantity of water absorbed was 18.189 per cent. If we consider that before absorbing this quantity of water it had first displaced it, the specific gravity of the mineral, supposing it to have

^{*} Pogg. Annal. cv. 144.

† We have deducted the foreign matters and hygroscopic water, and reduced the residue to the standard of 100 parts.

absorbed nothing, would therefore be 2.232. According to Smithson, the specific gravity of zinc bloom is 3.59.

CHEMICAL COMPOSITION OF THE SILICATES OF ZINC.

Pisolithic Amorphous Silicates.—We shall first speak of the pisolithic silicates, the formation of which is described at page 10. Some of these balls are opaque, and consist of beautifully concentric shells; but nearly all that we have examined contained a semi-translucent opal-like nucleus, often not bigger than a pin-head, but sometimes as large as the largest-sized peas; sometimes spheroidal balls, as large as beans, of this opalescent silicate, are found. These opalescent nuclei and balls are not, like the opaque ones, composed of concentric layers, but appear to be quite homogenous. The concentrical structure, as well as the opacity, may, perhaps, in some cases be explained as a process of drying, or dehydratation, and not as a successive growth; in favour of this view is the fact, that the opalescent nucleus has generally somewhat more water than the opaque external shell. In some cases this explanation does not certainly apply; for the nucleus has a different composition from the opaque shells, and the latter have all the appearance of having been successively formed about the former—the external surfaces of some of the shells having different lustres, for instance. The following are the results of the analyses of several of these balls:-

I.—Slightly spheroidal ball, not found as a nucleus, but may have been originally in a large ball; lustre resinous, inclining to vitreous; fracture conchoidal and shining; colour, milk-white; semi-translucent; brittle; sp. gravity, 3.694; not unlike opal, but not iridescent.

II.—A remarkably round ball, 6 to 7^{min} in diameter, pure enamelwhite; surface smooth, exactly like glazed porcelain, or fused white enamel; fracture like biscuit porcelain.

III.—Ball of about the same size as No. II., but having a dull surface; colour, enamel-white; fracture like biscuit porcelain.

IV.—A pea, 5^{mm} in diameter, taken from the centre of a large ball 10^{mm} in diameter; external surface smooth, like fused enamel; fracture like biscuit porcelain; colour, pure enamel-white; streak, white; hardness, 3·5; sp. gravity, 2·883. It contained in the centre a semi-translucent nucleus, about the size of a mustard-seed, of the density and other

properties of No. III.

rr		_			T	II.		III.	īv.
Oxide of zinc	3,				64·549	61.865		62.266	66·84 4
Silicic acid,					6.493	8.292		9.214	17.471
Carbonic acid	l,				11.246	11.301		10.101	4.637
Iron in com with phosp	ıbiı hoı	nat ic	ion aci	d,	0.003	0.002		0.003	0.002
Lime,				•	0.006	traces		0.001	traces.
Magnesia, Alkalies,					traces	traces	•	traces	traces.
Water,									
					99.969	100.084		100.947	99.788

M. Terreil also examined one of these siliceous balls; it had the specific gravity 2.762, and appears to have been analogous to No. IV. in other respects. As he could not remove the carbonate by means of very dilute acetic acid without also decomposing the silicate, he concluded that the two were in chemical combination. The specimen he examined contained 12.92 per cent. of water, of which 5.16 per cent. was driven off between 100° and 200° per cent.; he accordingly reckons this part as hygroscopic water. Considering silica to be a teroxide, he assumes the formula [ZnO,SiO₃, (ZnO,HO)³]² + ZnO,CO₂. This is a very complex formula, in which we have to assume the combination of silicate of zinc with hydrate of zinc, and the combination of this compound with anhydrous carbonate of zinc. We also believe that the carbonate is in combination with the silicate; but having had a greater variety of specimens to examine, we have, as we believe, arrived at a simpler expression of their composition. The following are the formulæ which we propose for the compounds examined by us:—

The following table shows the accordance between the theoretical composition calculated from the formulæ, and the results found:—

	I.	
	Calculated.	Found.
8 ZnO, .	. 64.598	. . 64.549
SiO_2 , .	. 6.165	6.493
3 CO ₂ , .	$13.126 \}_{29.235}$	$\frac{12.246}{10.070}$ 28.918
9 HO, .	16.109 $^{29.235}$	16.672 28.918
		99.960
	11.	
	Calculated.	Found.
6 ZnO, .	62.365	61.865
SiO, .	. 7.936	8.292
2 CO ₂ , .	11.0647	11:301)
8 HO, .	11^{204} $29 \cdot 697$. $18 \cdot 433$	$\cdot \cdot \cdot \frac{18.624}{18.624} \frac{29.925}{}$
		100.082
	Calculated.	Found.
10 ZnO, .	. 61.515	62.266
2 SiO ₂ , .	. 9.393	9.214
3 CO ₂ , .	. 10.000] 20.000	10.101
14 HO, .	19.090 29.090	10^{101} 19.362 29.463
		100.943

					٧.		
	ć	alculated.			_		Found.
6 ZnO,		66.996					66.844
2 SiO2,		17.051					17.471
CO ₂ ,		6·056\ 9·900}	15.0	056			10.834 15.471
4 H O,	•	9.900∫	10	900			10.834
							99.786

Nothing can be simpler than the connexion which these formulæ establish between the composition of the different balls. to them, they are compounds of two bodies, which are already well known, and one of which abounds in the locality, namely, calamine or hydrated silicate of zinc, and a dicarbonate of zinc, which may be precipitated by sesquicarbonate of soda, from a solution of sulphate, and which has been obtained by Boussingault combined with water as 2(2ZnO,CO₂) + 3HO; and by Schindler, 2ZnO,CO₂ + 2HO. The brief description which we have given in the first part of this paper of the circumstances under which these minerals occur, is sufficient to show that all the conditions for the formation of such a dicarbonate in the presence of a solution of silicate of zinc coexist. If these formulæ be correct, dicarbonate of zinc and disilicate of zinc are isomorphous; * and these compounds are analogous to those formed by bisulphate of potash and bichromate of potash, sulphate of potash, and chromate of potash, and the nitrates of potash and silver; and, consequently, similar compounds may be formed in endless proportions. Perhaps some of the zinc ores from Wiesloch, analysed by C. Riegel, may belong to this category; indeed, the affinity of silicate of zinc for carbonate of zinc, appears to be considerable. Almost every specimen of the former contains carbonic acid, even the transparent fibrous kinds.

Fibrous Hemimorphite, or Hydrated Disilicate of Zinc (Calamine).—
After discovering the simple relationship of the formulæ of the balls containing different proportions of water, the idea at once suggested itself to us that the isomorphism of the disilicate and dicarbonate might explain the want of atomic relation of the water, which is almost invariably observed in all the specimens of calamine that have hitherto been analysed. In order to test this hypothesis, we analysed a specimen of perfectly colourless (and in small pieces transparent), fibrous, hydrated silicate of zinc, which is associated with the hydrocarbonate from Dolores mine. This specimen was found to contain carbonic acid, as will be seen by the following table:—

^{*} See the paper "On the Action of Heat upon Silicates of Zinc," infra, for an account of some curious phenomena which appear to corroborate this view in a very remarkable manner.

[†] Archiv. d. Pharm. (2) Bd. lviii., p. 29, quoted by Bischoff—Lehrbuch der Chemischen Geologie 2^{ter} Bd. p. 1883.

Oxide of	zin	c,				67.792
Silicic aci	id,					$23 \cdot 424$
Carbonic	acio	ł,				1.421
Water,						7.263
						99.900

If we look upon the carbonic acid as existing in a compound 2 ZnO, CO₂, HO, that is in a corresponding degree of hydration to that in which silicate of zinc is found, the proportions in which the silicate and carbonate in the mineral will be found to be, in 100 parts:—

2ZnO,SiO ₂ ,HO, 2ZnO,CO ₂ ,Ho,	•	•	•	92· 7 02 7·2 98
				100:000

7.298 of this hydrocarbonate would contain:-

ZnO,				5.296
CO ₂ ,				1.421
				0.581
				7.208

If we deduct these numbers from those given above in the table of the results of the analysis of the mineral, we shall get the following proportions, which represent the quantities of oxide of zinc and water which belong to the silicate, as distinguished from those which belong to the carbonate:—

ZnO,				62.596
SiO ₂ ,				23.424
				6.682
				02:709

Or in 100 parts, and compared with the composition of silicate of zinc calculated from the formula $2ZnO,SiO_2,HO:$ —

		lculated fro he Formula	Calculated from the Analysis.			
2ZnO,	_	67.213			67.523	
SiO ₂ ,		25.409			25.268	
HO,		7.377			7.207	
		99.99			99.998	

The ratio between the number of equivalents of silicate and carbonate deducible from the preceding calculations is about 11:1; so that the pure white, fibrous silicate may be classed in the same category as the siliceous balls, and the formula $11(2ZnO,SiO_2,HO) + ZnO_2CO_2,HO$, assigned to it. In this case we have distributed the water between the

two constituent compounds; but we have not done so in the former, as it is probable that the water exists in two conditions—as basic water, and as saline water. Until we shall have further evidence on this point, however, we prefer writing the formulæ of the balls as above.

This power of combining in endless proportions appears to us not only to show that hemimorphite and dicarbonate of zinc are truly isomorphic, but that the isomorphism of carbon and silicon extends to carbonic and silicic acids, and thus adds an additional support to the view that silicic acid is a deutoxide.

Globular Radiated Hydrated Disilicate of Zinc.—Among the minerals which were procured at the mines of Florida, was a very peculiar variety of silicate of zinc. It consisted of an irregular mass, sometimes distinctly botryoïdal, of globular silicate,—the largest of the globules being about a centimètre in diameter. Externally the globules were covered with asperities, which were the ends of crystals disposed in a radiated acicular The fracture of a globule showed the cleavage planes of these crystals, arranged in a stellated form, and inclined to each other. These cleavage planes were large, and appeared to be $\infty P \infty$, parallel to which the cleavage is complete. Colour, yellowish-brown; the fresh surfaces being studded with a number of extremely small black points. The cleavage planes had a mother-of-pearl lustre, which soon tarnished, and became dull; sp. gr. 3.267. When freshly fractured, and a perfectly undecomposed fragment examined, its hardness was nearly = 5. The mineral decomposed into a brownish-yellow, ochry substance with remarkable facility. Its composition was found to be:-

Oxide o							
Silicic a	cid	,					24.883
Sesqui-	ixi	le o	fii	on,			5.182
Lime,							
Water,						,	7.121
							99.381

If we deduct the oxide of iron, and calculate the proportions in 100 parts of the oxide of zinc, silica, and water, alone, and compare the results with the theoretical composition deduced from the formula 2 ZnO, SiO₂,HO, we shall find that the silica and water are too high in the experimental results, and consequently the oxide of zinc too low. In what state is the sesquioxide of iron in this mineral? Is it in combination, or merely mixed mechanically with it? The property which silicate of zinc has of dissolving in a solution of caustic potash, suggested itself at once as a means of answering this question. On treating the mineral in the state of fine powder with a solution of potash in the cold during several days, the whole of the silicate of zinc was dissolved, and a reddish-brown powder was left; the composition of which may be represented by the formula $2\text{Fe}_2\text{O}_3$, SiO_2 , HO. This is exactly the silicate of iron, which is found in Glauber's iron-tree, obtained by

putting a piece of dried protochloride, sesquichloride, or protosulphate of iron, in a solution of silicate of potash:—

$$3(2\text{Fe}_2\text{O}_3\text{SiO}_2) + 2(\text{KO},\text{CO}_2).$$

This would, in all probability, be the silicate formed by the mutual decomposition of an alkaline silicate and sulphate, or bicarbonate of iron.

The great facility with which this mineral decomposes and behaves in acids, and its peculiarities generally, would seem to show that the silicates of zinc and iron are in some sort of combination, and not simply intermixed. If from the whole we deduct not merely the oxide of iron, but also the amount of silica and water combined with it, the remainder will contain oxide of zinc, silica, and water, in the proportions represented by the formula $2ZnO,SiO_2,HO$.

Perhaps many other minerals containing peroxide of iron, &c., would present us with a like phenomenon, if we could dissolve one constituent like the silicate of zinc. There are, no doubt, many cases where foreign substances cannot be considered to be merely mechanically mixed in a mineral, and yet cannot be held to replace some constituent isomorphically, which may be explained in this way. Indeed, it is probable, that many of the so-called isomorphic replacements are in reality such compounds, held by a very feeble affinity, but which, unlike the one here in question, cannot be dissected.

The Rev. Samuel Haughton, M.A., F.R.S., Fellow of Trinity College, Dublin, read the following paper:—

On a Graphical Mode of Calculating the Tidal Drift of a Vessel in the Irish Sea or English Channel. (Plate II.)

The change of level in the surface of tidal water, between two given hours, may be graphically calculated by the method given by Mr. Airy in his Treatise on Tides and Waves. Let a circle be described whose radius is half the Range of Tide, and painted on a vertical wall; the tide, in its rise and fall, will cover and uncover equal arcs of this circle in equal times. If this circle be divided like the dial of a clock, XII. and VI. corresponding to the top and bottom of the vertical diameter, and tidal hours be used, the rise or fall of the water may be easily calculated.

In calculating the Drift produced by the Tidal Stream, we are not given the total drift in six tidal hours, which would correspond to the Range of the Tide; but we have instead the maximum velocity of the Tidal Current at half-flood and half-ebb.

The following construction will enable us easily to calculate the Tidal Drift between two given hours:—

Let a circle be described whose radius is double the maximum rate of stream, and let this circle be divided into Tidal Hours; from the two given